

JUN 21 2006

1 TITLE: A Method, and Article of the Method, for Fabricating a  
2 Flexible, Hollow Waveguide.

4 Field of the Invention ← Center

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6 The present invention relates to waveguides and methods  
7 of making same, and more particularly to a flexible, rugged  
8 waveguide comprising a photonic, bandgap, hollow fiber,  
9 transmitting in the infrared and visible regions.

11 BACKGROUND OF THE INVENTION ← Initial Caps.

13 The flexible waveguide of this invention is based upon  
14 technology disclosed in United States Patent Nos. 5,815,627;  
15 issued: September 29, 1998; 5,567,471, issued: October 22,  
16 1996; and 5,440,664; issued: August 8, 1995, which technology  
17 and teachings are meant to be incorporated herein by way of  
18 reference. The aforementioned waveguide inventions have a  
19 common inventor, James Harrington, and a common assignee,  
20 Rutgers University. In aforementioned United States Patent No.  
21 5,815,627, it was taught that waveguides are capable of  
22 guiding both IR and visible radiation. This is also a  
23 distinguishing feature of this invention. This invention,

however, has fabricated a waveguide that can be tailored for use over a wide wavelength range by the use of multiple, uniform, film coatings deposited by liquid phase chemistry methods. The coatings of the inventive waveguide have an additive, are fabricated by an additive technique rather than a subtractive method, i.e. the former Ag layer as taught in the aforementioned patents, was originally depleted in part, with the establishment of the AgI layer. The AgI layer is totally absent in the present application. Even the Ag layer is only present in one embodiment thereof, and is but one selection of other metals used for the metallic underlay.

This invention utilizes dielectric layers of sulfide materials, which are built in stacked geometries to fashion unique waveguide structures.

The waveguides of the present invention can be fabricated in one of two novel ways:

- (a) The dielectric layers of cadmium and lead sulfide can be applied directly to the smooth bore surface of a silica glass tube; or

(b) The dielectric layers of the cadmium and lead sulfides can be applied to a metallic surface, for example, metals selected from a group consisting of Ag, Au, Cu, Pt, Ni, Pt, Mb, and Al, which has been smoothly coated upon the smooth inner bore of the silica glass tube.

A protective polymer coating is layered upon the outer surface of the tube in both embodiments. The dielectric layers of this invention comprise CdS and PbS, which form a unique compatibility pair, in which deposition of each material does not affect the underlying layer. These paired sulfides can be stacked in multiple, thin film layers to provide specific and unique characteristics. The sulfide layers are deposited using similar liquid-phase chemistry taught in the prior patents. The thickness of each layer can be tailored for use over a wide range of wavelengths. The measured losses for a single layer of CdS or a PbS film deposited over an Ag layer was in agreement with the prior Ag/AgI film studied at 10.6 $\mu$ m for applications using CO<sub>2</sub> IR lasers.

69 The CdS and PbS materials have disparate refractive  
70 indices with a ratio of about 2 to 1. This is often referred  
71 to in this technology, as the index contrast ratio. The high  
72 contrast of this layering makes possible a photonic bandgap  
73 hollow fiber. The deposit of the cadmium sulfide layer  
74 provides the transmission in the visible region.

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76 Discussion of Related Art:

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78 Prior-art hollow waveguides can provide poor beam quality  
79 (poor transverse spatial coherence). <sup>Figure</sup> FIG. 12B of Gregory &  
80 > Harrington, <sup>(see below cite) Figures</sup> and 5 and 6 of Croitoru et al.,  
81 "Characterization of hollow fibers for the transmission of  
82 infrared radiation", Appl. Opt. v. 29, 1805-1809 (20 Apr.,  
83 1990) and Dror et al., "Hollow Tubes for Transmitting IR Laser  
84 Energy for Surgery Applications", presented to ICALEO '89  
85 (15-20 Jan., Los Angeles), are representative of the  
86 characteristics of prior art hollow waveguides.

87 United States Patent Nos. 5,815,627; issued: September  
88 29, 1998; 5,567,471, issued: October 22, 1996; and 5,440,664;  
89 issued: August 8, 1995, depict Ag/AgI film waveguides.  
90 Typically, waveguides such as are disclosed in Matsuura &  
91 Miyagi, "Low-loss metallic hollow waveguides coated with

✓  
92 durable and nontoxic ZnS", Appl. Phys. Lett. v. 61, 1622-1623  
93 (5 Oct., 1992) is superior. Waveguides with metal tube walls  
94 that serve as the supporting structure for any coatings (such  
95 as disclosed in U.S. Pat. No. 5,005,944, issued to Laakman et  
96 al., and U.S. Pat. No. 4,913,505, issued to Levy '505) may be  
97 capable of handling substantial power, but are semi flexible  
98 at best. Those with plastic tube walls (such as disclosed in  
99 U.S. Pat. No. 4,930,863, issued to Croitoru et al.) are  
100 flexible, but have marginal power-handling capability at best  
101 and high loss. Yet-earlier devices such as disclosed in U.S.  
102 Pat. No. 3,436,141, issued to Comte, U.S. Pat. No. 3,583,786,  
103 issued to Marcatili, and U.S. Pat. No. 3,963,828, issued to  
104 Onoda et al., have not proven useful for the applications of  
105 present interest at the wavelengths of present interest.  
106

107 Hollow waveguide fibers having an index of refraction  
108 less than one, have not yet attained both transmission  
109 characteristics and flexibility required for many  
110 applications. However, in other respects these waveguide  
111 fibers are quite satisfactory at selected wavelengths. See  
112 Gregory & Harrington, "Attenuation, modal, and polarization  
113 properties of  $n < 1$ , hollow dielectric waveguides", Appl. Opt.  
114 v. 32, 5302-5309 (20 Sept., 1993). OK

115  
116 As aforementioned, the current invention is an  
117 improvement over the waveguide devices of the prior aforesaid  
118 Harrington patents.

119  
120 The present invention has made loss measurements at key  
121 laser wavelengths, e.g. as a CO<sub>2</sub> laser waveguide. The current  
122 invention provides a flexible, hollow, waveguide, and method  
123 for making same. The waveguide tube meets the need for a  
124 flexible, visible and IR region, laser transmission medium  
125 having a relatively low loss.

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130 SUMMARY OF THE INVENTION — *Initial Caps*

131  
132 In accordance with the present invention, there is  
133 featured a flexible, hollow waveguide for the transmission  
134 of radiation in the infrared and visible regions, and a  
135 method of making same. The waveguide comprises a hollow,  
136 flexible, silica-glass tube having a transparent annular  
137 body defining a bore with a smooth inner bore surface. In

138 a first embodiment, a reflective, thin film, metallic  
139 layer, consisting of a metal selected from a group of  
140 metals consisting of: Ag, Au, Cu, Ni, Pt, Mb, Zn, and Al,  
141 is coated upon the smooth inner bore surface of the silica-  
142 glass tube. A single, thin film cadmium sulfide dielectric  
143 layer, or a pair of thin film dielectric, cadmium and lead  
144 sulfide layers respectively, are then disposed upon said  
145 reflective layer. Cadmium sulfide transmits radiation in  
146 both the visible and infrared region. This pair of sulfide  
147 layers has disparate refractive indices with a ratio of  
148 approximately 2 : 1, which is vital to provide high  
149 contrast, and to fabricate a photonic, bandgap, hollow  
150 waveguide tube. In a second embodiment, no metallic layer  
151 is used, and the pair of thin film cadmium and lead sulfide  
152 layers is multiply stacked directly upon the smooth, inner  
153 bore of the silica-glass tube.

154  
155 The thin films are deposited using dynamic wet chemistry,  
156 and the thickness is tailored to minimize the attenuation  
157 of the waveguide over specific infrared wavelengths.

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159 It is an object of the present invention to provide ~~a~~ an  
160 improved flexible, hollow waveguide.

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It is another object of this invention to provide a flexible, hollow waveguide comprising a photonic, bandgap hollow fiber.

It is yet a further object of the current invention to provide a flexible, hollow waveguide, which transmits radiation in both the visible and infrared region.

BRIEF DESCRIPTION OF THE DRAWINGS

*Initial  
Caps*

A complete understanding of the present invention may be obtained by reference to the accompanying drawings, when considered in conjunction with the subsequent detailed description, in which:

FIGURE 1 depicts the growth kinetic graph of the thin films deposited in the Ag coated 1,000- $\mu$ m bore waveguide;



FIGURE 2 shows the graph of the UV-VIS spectra of a  
1,000- $\mu$ m bore Ag/CdS waveguide

FIGURE 3 illustrates the graph of the FTIR spectra of a  
1,000- $\mu$ m bore Ag/Pbs waveguide;

FIGURE 4 depicts a graph of the cross-sectional FESEM  
image of a 1,000- $\mu$ m bore Ag/CdS/PbS waveguide;

FIGURE 5 shows a graph of the FTIR spectra of a 1,000- $\mu$ m  
bore of Ag/CdS and Ag/PbS, Ag/CdS/PbS and Ag/CdS/PbS/CdS  
waveguide;

FIGURE 6 illustrates a partial schematic view of the  
first embodiment of the waveguide of this invention;

FIGURE 6a depicts a partial schematic view of the second  
embodiment of the waveguide of this invention;

205 DESCRIPTION OF THE PREFERRED EMBODIMENT ← *Intem*  
206 *Caps*

207 Generally speaking, a flexible, hollow, waveguide is  
208 featured, that functions in the infrared and visible regions.  
209 The waveguide comprises a hollow, flexible, silica-glass tube  
210 having a smooth bore that is coated in one embodiment with a  
211 reflective, metal substance on the inner bore surface. A pair  
212 of sulfide materials respectively of cadmium and lead sulfide,  
213 is then layered over the reflective substance. The sulfide  
214 materials form a high contrasting refractive index of  
215 approximately 2 : 1, thus creating a photonic, bandgap tube.  
216 In a second embodiment, the metallic layer is not used, and  
217 the pair of sulfide layers is singularly or multiply stacked  
218 directly upon the bore.

219  
220 There are two embodiments of the invention. The first  
221 embodiment fabricates the waveguide by liquid phase deposition  
222 of a metallic, reflective layer, usually Ag upon the smooth  
223 inner bore surface of the silica-glass tube. Other metals of  
224 choice such as Au, Cu, Ni, Pt, Zn, Mb, Al, etc., can also be  
225 used. Then, a single or pair of sulfide-containing  
226 dielectrics is coated over the metal. In the second  
227 embodiment of the invention, no metallic or reflective layer

228 is deposited, and only pairs of sulfide-containing dielectric  
229 films are coated upon the smooth inner bore.

230

231 Now referring to <sup>Figure</sup>~~FIGURE~~ 6, a first embodiment of the waveguide  
232 1 of this invention is illustrated. The waveguide 1,  
233 comprises a silica-glass tube 3, having a thin-wall of  
234 approximately 50 to 200 microns wall thickness, and a smooth  
235 inner bore. A reflective, metallic layer 4 is coated over the  
236 smooth bore using liquid phase chemistry, as taught in the  
237 aforementioned patents. The reflective layer may comprise Ag,  
238 Au, Ni, Cu, Al, Pt, Zn, Mb, etc. A single layer of cadmium  
239 sulfide, or paired sulfide composite of cadmium sulfide and  
240 lead sulfide, respectively, is layered over the reflective  
241 layer 4. The sulfide composite comprises respective layers 5  
242 and 6, of cadmium and lead sulfides. <sup>, respectively.</sup> The sulfide materials  
243 form a high contrast, refractive index of approximately 2 : 1  
244 creating a photonic, bandgap tube. The silica-glass tube 3 is  
245 covered with an outer layer 2 of plastic for protection.

246

247 Referring to FIGURE 6a, a waveguide <sup>1a</sup>~~10~~ is shown having a  
248 flexible, hollow, silica-glass tube <sup>3,</sup>~~11~~ upon which is stacked  
249 at least one pair of cadmium and lead sulfide layers <sup>5,</sup>~~12~~ and  
250 <sup>6,</sup>~~14~~, respectively. A multiplicity of pairs of cadmium and lead

251 sulfide layers <sup>5</sup>~~12~~ and <sup>6</sup>~~14~~ can be deposited over the first pair,  
252 as shown in phantom.

253 Examples: No Bold

256 1. A smooth, inner bore surface 3 of a flexible  
257 hollow tube 2 of a waveguide 1, is coated with a  
258 metallic, reflective layer 4 of silver. The  
259 silver layer 4 was then coated with cadmium  
260 sulfide to form layer 5, and then coated with  
261 lead sulfide to form layer 6. Each layer was  
262 coated using liquid phase chemistry, utilizing a  
263 peristaltic pump. The flow rate of the  
264 solutions through the hollow tube was chosen at  
265 30 ml/min.

266 The cadmium sulfide coating was applied over  
267 the Ag coating, using one of the two chemical  
268 baths.

269 1. I) Cadmium Nitrate 0.1 M, II) thiourea 0.5 M -  
270 this is considered a full concentration  
271 solution. For most depositions, the  
272 concentration was reduced to 1/2 to 1/6 the  
273 full concentration.

274 2. I) Cadmium acetate 5mM, II) thiourea 100mM.

275  
276 All the coating solutions were prepared in  
277 distilled and deionized water. The solutions are  
278 prepared using an ultrasonicator or a magnetic  
279 stirrer.

280 The Cd ion containing solution is complexed  
281 with ammonium hydroxide solution. Initial addition  
282 of ammonia will form a white precipitate of  $\text{Cd}(\text{OH})_2$   
283 and the solution becomes turbid. With further  
284 addition of ammonia dissolves the white precipitate  
285 and forms a soluble Cd-ammonia complex. The solution  
286 pH is maintained between 10 and 13 using sodium  
287 hydroxide solution and nitric acid as titrating  
288 agents. The second solution of sulfide ion is  
289 prepared by dissolving thiourea in water. The two  
290 solutions were then flowed through the hollow tube  
291 and coated the Ag. The complexed Cd ion solution  
292 reacts with the sulfide ion containing solution to  
293 deposit <sup>a</sup> thin film of CdS. The hollow tube was dried  
294 in flowing air.

295 2. For deposition of PbS thin films, lead nitrate was  
296 used as the source of Pb ions and thiourea or a mix of

297 thiourea and thioacetamide was the source of sulfide  
298 ions. All the solutions were prepared in distilled and  
299 deionized water (DI). The solutions are prepared using  
300 an ultrasonicator or a magnetic stirrer. The chemical  
301 bath used for the deposition of lead sulfide is as  
302 given below:

303 Solution 1: A)  $\text{Pb}(\text{NO}_3)_2$  : 4g / 500 ml; b) NaOH: 12

304 > g/500ml, and

305 Solution 2: thiourea: 6g/ 1000 ml or thiourea 4g and  
306 thioacetamide 2 g to 1000ml of water.

307 The NaOH solution is slowly added to the  $\text{Pb}(\text{NO}_3)_2$   
308 solution while continuing to stir. Initially the  
309 solution turns turbid due to the precipitation of  
310  $\text{Pb}(\text{OH})_2$  which dissolves to form a soluble Na-Pb-  
311 hydroxide complex on further addition of NaOH. The  
312 complexed lead ion reacts with a sulfide ion in  
313 solution to form PbS. Deposition of PbS requires that  
314 the solutions containing Pb and S ions are  
315 supersaturated in order to precipitate out in solution  
316 and nucleate heterogeneously on the substrate. The  
317 bore surface of the waveguide was coated with the  
318 solutions using the peristaltic pump as previously  
319 shown. Surfaces were air dried.

3. Infrared and visible region investigation of Ag/CdS, Ag/PbS, Ag/CdS/PbS and Ag/CdS/PbS/CdS waveguides, as can be observed with reference to the FIGURES 1 through 3 and 5, will now be described.

In the original work on omni directional waveguides authored by Fink, et al. <sup>(insert reference "3" info. from p. 26)</sup> an all-dielectric structure of alternating low/high index films was described. In this invention, use of a metallic film in conjunction with a multilayer dielectric stack means that the waveguide will need fewer dielectric layers to achieve the same loss as an all dielectric omni directional structure. CdS and PbS films are transparent in the 2 to 12  $\mu\text{m}$  region. The refractive indices of CdS and PbS are 2.25 and 4.27 at 1.55  $\mu\text{m}$  and 2.25 and 4.0 at 10.6  $\mu\text{m}$ , respectively. This gives an index contrast of  $4.27/2.25 = 1.9$  at 1.55  $\mu\text{m}$  and 1.78 at 10.6  $\mu\text{m}$ . These two dielectric materials and other sulfides such as ZnS and ZnSe may be deposited in thin film form using straightforward solution chemistry methods. <sup>(insert refs. 4+6 from p. 26)</sup> Furthermore, these two materials are compatible, and the wet chemistry methods used to deposit both films are similar. <sup>(insert refs. 7+8 from p. 26)</sup>

Dielectric-coated metallic hollow waveguides of this invention are designed to minimize the attenuation of the waveguide over a particular IR wavelength region by optimizing the thickness of each dielectric layer. The well-established theory of Miyagi and Kawakami<sup>19</sup> (insert ref. 9 from page 27) was used to calculate the expected losses for multilayers of CdS and PbS coatings. Using this theory, and the n and k values for CdS and PbS, the losses for single and multilayer films at both 1.55 and 10.6  $\mu\text{m}$  were calculated. The calculations at 10.6  $\mu\text{m}$  show that a 1,000- $\mu\text{m}$  bore of a hollow glass waveguide with a 3-layer <sup>stack</sup> ~~stage~~ of CdS/PbS/CdS films deposited over Ag will have a straight loss of 0.016 dB/m compared to a straight loss of 0.07 dB/m for a single layer CdS film deposited over Ag. That is, the calculated attenuation coefficients are approximately four times less for the three layer design, compared to a single dielectric layer at 10.6  $\mu\text{m}$ ,

As aforementioned, hollow glass waveguides are prepared in a two step process in which an Ag film is first deposited on the inner surface of the silica tubing and then a dielectric layer of CdS or PbS is deposited on top of the metallic layer. For multilayer dielectric structures, sequential deposition of alternating low/high films leads to the structures, Ag/CdS, Ag/CdS/PbS, and Ag/CdS/PbS/CdS. The Ag film is deposited on the inner surface of the silica tubing using a liquid-phase reduction



ART  
365 reaction typical of that used in the prior patents to Harrington,  
366 using Ag/AgI hollow glass waveguides <sup>(10-12)</sup>. ~~(insert refs 10, 11, 12 from p. 27)~~ The thickness of the  
367 Ag film is chosen to be sufficiently thick to prevent any  
368 transmission through the film, but thin enough so that the  
369 surface roughness is as low as possible. Specifically, the  
370 thickness of the Ag film is chosen to be at least ten times the  
371 skin depth at 10.6  $\mu\text{m}$ . The skin depth of an Ag film at 10.6  $\mu\text{m}$   
372 is 12 nm. In all the experiments CdS and PbS have been deposited  
373 on Ag films that vary in thickness from 150 to 200 nm. At this  
374 thickness the Ag films are quite smooth ( $< 12$  nm rms roughness)  
375 and, therefore, they provide a good surface for the deposition of  
376 the dielectric layers. A very important feature of the CdS and  
377 PbS coatings is that they are additive and, thus, independent of  
378 the Ag film. This is in strong contrast to the waveguides made  
379 using AgI coatings ~~(insert refs. 11, 12, and 14 from p. 27-28)~~ AgI is deposited in a subtractive  
380 process in which AgI is formed by the diffusion of iodine ions  
381 into the underlying silver film. Therefore, to produce a thick  
382 dielectric layer of AgI will require a thick starting layer of  
383 Ag. In ~~the~~ <sup>an</sup> article by Rabii and Harrington <sup>they</sup> ~~(insert 15 from page 28)~~ have shown that the  
384 surface roughness of both the Ag and the AgI film increases with  
385 increasing thickness of the Ag layer.

386  
387 Additional Examples:

move to  
next page. NO bold

388

389 As aforementioned, CdS and PbS thin films were deposited using

390 a wet chemistry deposition technique<sup>(Sugent 4 line p. 26)</sup>. Cadmium nitrate and

391 cadmium acetate are used as the source of Cd ions; lead nitrate

392 the source of Pb ions; and thiourea,  $(SC(NH_2)_2)$ , the source of S

393 ions. It is important to accurately control pH of these

394 solutions, since the CdS and PbS precipitates are stable only in

395 the pH range 10 to 13. <sup>The</sup> pH control and chelating is achieved

396 using an ammonia solution for CdS and sodium hydroxide for PbS.

397 Specifically, the pH for aqueous  $Cd(NO_3)_2$  is maintained between 11

398 and 12. Owing to the fact that the reaction rate also changes

399 with the pH, it is necessary to calibrate the process for a given

400 pH range. The thickness of both CdS and PbS increases with

401 increasing concentration of Cd, Pb and S ions in solution and

402 with increasing deposition time. From a study of the growth

403 kinetics for both CdS and PbS thin films, it has been

404 established, that the optimal concentration and flow rate

405 conditions for uniform film deposition for tubing require lengths

406 greater than 1.5 m. The best coatings were made using  $> 0.01$  M

407 solutions and pumping rates of 30 ml/min.

408

409 The multilayer dielectric structures of Ag/CdS/PbS and

410 Ag/CdS/PbS/CdS, were prepared in a manner similar to the single-

layer dielectric metallic waveguides. The different layers were coated in a sequential manner with an intermediate drying step after coating each layer. An Ag-only tube was coated with a single layer of either CdS, or PbS, when the 2- and 3-layer structures were being coated as an independent check on the thickness for each layer.

No bold  
highlighting

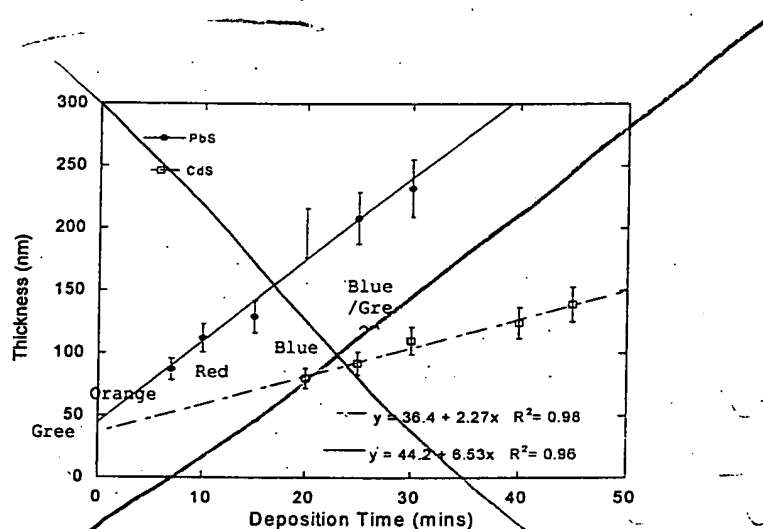
### Optical characterization of Ag/sulfide film Waveguides;

The spectral characteristics of the Ag/CdS and Ag/PbS hollow glass waveguides were evaluated using a Perkin Elmer UV-VIS spectrometer, and Nicolet Protégé FTIR. A typical spectral response shows interference peaks, which depend on the thickness of the dielectric thin films. The thickness of a single layer dielectric, "d", was calculated from the peak position of the longest-wavelength interference band,  $\lambda_p^{(m)}$ , using the relation

$$d = \frac{m \cdot \lambda_p^{(m)}}{4 \cdot \sqrt{n^2 - 1}} \quad (1)$$

where m is the order of the interference maxima ( $m=1$  for the longest-wavelength band);  $\lambda_p$  is the wavelength of the  $m^{\text{th}}$  absorption peak; and  $n_1$  is the refractive index of the dielectric film. From ~~Eq.~~ <sup>Equation</sup> (1) it is observed, that the peak position shifts to longer wavelengths as the thickness of the film

increases. Spectral data has been used to determine the thickness of films prepared using different growth kinetics. The film thickness obtained from the optical measurements has then been correlated with direct thickness measurements using a field-emission scanning electron microscope (FESEM). In this way one obtains the growth kinetic curves for CdS and PbS deposited on Ag, <sup>as</sup> shown in Fig. 1. Figure 1.



In Figure 1, the growth kinetic curves of the CdS and PbS thin films deposited in a Ag coated, 1,000  $\mu$ m bore Hollow Glass Waveguide, are shown.

datum points of curves 60 and 62 represent  
regions  
 The color indicated is the color that one would see looking through the waveguides with an optical microscope, and are representative of film thickness.

All films were prepared using 0.01 M solutions and a flow rate of 30 ml/min. The growth kinetics curves in Figure 1 indicate that

CdS (open symbols) has a slower growth rate on Ag compared to PbS (solid symbols) under similar conditions. The reason for the slower growth rate for CdS compared to PbS, is that the CdS complexes with the ammonia used in the deposition and this decreases the rate of deposition. The data also shows that the thickness of both dielectrics increases linearly with time, with growth rates of ~ 2.3 and 6.9 nm/min for CdS and PbS, respectively. The mechanism for linear growth is based on the Stranski-Krastanov model of island-like growth. This mechanism involves nucleation and growth in the linear growth region. This information is important as we need to carefully control film thickness for single and multilayer structures. The UV-VIS spectra for the Ag/CdS is given in Figure 2, and the FTIR spectra for the Ag/PbS in Figure 3. The spectral data clearly show that the position of the interference peaks shifts to longer wavelengths as the thickness of the film increases as predicted by Equation (1). It has been observed relative to Figure 2, also noted from the insert photos in Fig. 2, that the Hollow Glass Waveguides show a color variation. This is due to selective filtering of the input white light by the thin film coating (interference effect). This color variation is seen with the CdS coatings, but not the PbS films, because these films do not transmit well at visible wavelengths.

The thickness of the thin films was obtained by direct measurements using a FESEM. A photomicrograph taken with the FESEM for a typical cross-section of the thin film combination on a silica substrate 44 of identified as 45, 46, and 47, respectively Ag/CdS/PbS is shown in Figure 4. The CdS film appears darker than the PbS film, because the in-lens detector produces a negative image of the secondary electron image. Also, the silica substrate 44 is a portion of the tube 3. The thicknesses of the films shown in Figure 4 are; Ag 154 nm, CdS  $169 \pm 16$  nm, PbS  $82 \pm 6$  nm. Degradation was not observed for the underlying film, when the new film is deposited over it. That is, CdS and PbS do not react with each other during the deposition of successive layers. The film thickness measured from the FESEM micrographs of both single and multilayer dielectric film are summarized in Table below. These results agree very well with the optical thickness measurement.

Table 1. Thickness values for CdS and PbS thin films on Ag determined from FESEM images

Thickness of	Thickness of	Thickness of
HGWs	Ag	PbS
	nm	nm
Ag/CdS	156	$172 \pm 16$
Ag/PbS	158	$96 \pm 16$
Ag/CdS/P	154	$82 \pm 6$
	22	

489

490 A series of 1,000- $\mu$ m-bore HGWs with 1, 2, and 3 dielectric layers

491 deposited over Ag were fabricated using wet chemistry methods [8,

492 11]. The spectral losses for these straight waveguides are shown

493 in ~~Fig. 5~~ <sup>Figure</sup> 5. From ~~Fig. 5~~ <sup>Figure</sup>, it may be seen that the addition of each

494 dielectric layer shifts the interference peaks <sup>56, 57, 58, respectively,</sup> to longer

495 wavelengths. This is a result of the increase in thickness with

496 each additional layer.

497

498 The thickness of each dielectric layer was determined from a <sup>witness</sup> ~~wi~~

499 sample composed of each dielectric layer deposited separately on

500 <sup>a slide.</sup> ~~These~~ witness samples were deposited along with the multilayer waveguides.

501 From the witness samples we determined the thickness of the <sup>individual</sup> ~~indiv.~~

502 layers using the position of the long wavelength interference peak

503 <sup>from Equation</sup> (1). The thicknesses obtained were; Ag 200 nm, CdS (adjacent to

504 <sup>Ag</sup> 156 nm, PbS 87 nm, and CdS (next to air) 97 nm. The thickness value

505 CdS and PbS layers measured optically agree very well with <sup>FESEM</sup> ~~with~~

506 measurements and are within experimental errors as shown in Table 1. <sup>from</sup> ~~Figure~~

507 ~~Fig. 5~~ <sup>Figure</sup> we see that this waveguide is best suited for operation beyo

508 <sup>5</sup>  $\mu$ m. <sup>nd</sup>

509 <sup>than</sup> Losses measurements were made at 1.55  $\mu$ m using a diode laser rather

510 a CO<sub>2</sub> laser at 10.6  $\mu$ m where the HGWs would ultimately be most <sup>used</sup> ~~use~~

511 The reason for using a 1.55  $\mu$ m laser was that we were <sup>interested in</sup> ~~interested~~

mm

512 developing a new waveguide for secure communication systems at 1.55  
513 Clearly, solid-core silica fibers are a better choice for  
514 <sup>most</sup> applications at 1.55  $\mu\text{m}$ . The output of the diode laser was <sup>via</sup>  
515 <sup>a</sup> pigtailed single mode fiber terminated with a Selfoc lens. The <sup>spectral</sup>  
516 response of the HGWs chosen for loss measurements was similar to  
517 <sup>that</sup> shown in <sup>Figure</sup> ~~Fig.~~ 5. In general, coating thicknesses were not optimized  
518 <sup>for</sup> lowest loss at 1.55  $\mu\text{m}$ ; however, as may be seen from the cut-back <sup>measured</sup>  
519 data given in Table 2, <sup>(see below)</sup> the losses were still quite low. <sup>calculated</sup>  
520 losses in Table 2 may be compared to the theoretical losses <sup>calculate</sup>  
521 <sup>at</sup> both 1.55 and 10.6  $\mu\text{m}$  using the n and k values of the dielectric <sup>(insert 9 from p. 27)</sup>  
522 <sup>films</sup> and the theory of Miyagi and Kawakami [9]. The losses at 1.55  $\mu\text{m}$  are <sup>(k=0.39)</sup>  
523 <sup>high</sup> when PbS is used because k is rather large at this wavelength <sup>(k=0)</sup>.  
524 At 10.6  $\mu\text{m}$  k for PbS is 0.008 and the calculated loss for <sup>Ag/CdS/PbS/CdS</sup> ~~Ag/CdS/PbS~~  
525 is over four times less than for Ag/CdS. The bending losses for  
526 <sup>the</sup> waveguides were not measured. It is well known that there is <sup>which</sup>  
527 <sup>an</sup> additional loss on bending for non-omni directional waveguides, <sup>(insert 17 from p. 28)</sup>  
528 varies as  $1/R$ , where R is the radius of the bend <sup>[17]</sup>. Since <sup>that we</sup>  
529 <sup>our</sup> waveguides have no more than 3 dielectric layers it is expected <sup>that we</sup>  
530 would not observe omni directional behavior rather there would <sup>be</sup>  
531 <sup>an</sup> added loss on bending.

532 Table 2 Loss values for 1,000- $\mu\text{m}$  bore HGWs with 1, 2, and 3-layer  
533 dielectric coatings.

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table  
on next page



↓ ? ? ? ↓

↓ ?

534	<del>4</del>	Multilayer	Measured l, μm,	Theoretic 1.55 μ	Theoretic 10.6 μ	Conclusions summary
536	(We	Ag/CdS	0.2 ±	2.7	7.0	(have
		Ag/PbS	0.26 ±	2.5	7.3	
		Ag/CdS/PbS	0.1 ±	8.6	3.3	
		Ag/CdS/PbS/Cd	0.06 ±	6.7	1.6	

↓

545 demonstrated that liquid-phase chemistry methods can be used to

546 deposit good optical quality CdS and PbS thin films to form both

547 single and multiple dielectric/metallic HGWs. The spectral response

548 for waveguides with these films deposited over Ag show well defined

549 interference bands indicating good film thickness uniformity over the

550 entire length of the guide. Varying the deposition time controls the

551 position of the interference peaks. Furthermore, we have found that

552 CdS and PbS are compatible and the deposition of each material does

553 not affect the underlying film. In this way the thickness of each

554 layer in the multilayer stack can be tailored for use over a wide

555 wavelength range. The final 3-layer stack showed that it is possible

556 to make a multilayer coating but we have yet to reduce the

557 attenuation to the level predicted by theory. Moreover, the measured

558 losses for the single-layer CdS or PbS films at 1.55 μm are in

559 general agreement with the well studied Ag/AgI HGWs at 10.6 μm [14].

560 In reality, the greatest potential for these waveguides is likely to

(Insert 17 from p. 28)

561 be at 10.6  $\mu\text{m}$  for applications involving CO<sub>2</sub> laser power delivery and  
562 IR fiber sensors.

563  
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619 <sup>P</sup> Since other modifications and changes varied to fit  
620 particular operating requirements and environments will  
621 be apparent to those skilled in the art, the invention is  
622 not considered limited to the example chosen for purposes  
623 of disclosure and covers all changes and modifications  
624 which do not constitute departures from the true spirit  
625 and scope of this invention.

626  
627 Having thus described the invention, what is desired to  
628 be protected by Letters Patent is presented in the  
629 subsequently appended claims.

630  
631 ~~What is claimed is:~~

# DRAWINGS

CdS and PbS thin films were deposited using a wet chemistry deposition technique [4]. Cadmium nitrate and cadmium acetate are used as the source of Cd ions; lead nitrate the source of Pb ions; and thiourea,  $(SC(NH_2)_2)$ , the source of S ions. It is important to accurately control pH of these solutions since the CdS and PbS precipitates are stable only in the pH range 10 to 13. pH control and chelating is achieved using an ammonia solution for CdS and sodium hydroxide for PbS. Specifically, the pH for aqueous  $Cd(NO_3)_2$  is maintained between 11 and 12. Since the reaction rate also changes with the pH, it is necessary to calibrate the process for a given pH range. The thickness of both CdS and PbS increases with increasing concentration of Cd, Pb and S ions in solution and with increasing deposition time. From a study of the growth kinetics for both CdS and PbS thin films, we have established optimal concentration and flow rate conditions for uniform film deposition for tubing with lengths greater than 1.5 m. The best coatings were made using  $> 0.01$  M solutions and pumping rates of 30 ml/min.

The multilayer dielectric structures of Ag/CdS/PbS and Ag/CdS/PbS/CdS, were prepared in a manner similar to the single-layer dielectric metallic waveguides. The different layers were coated in a sequential manner with an intermediate drying step after coating each layer. An Ag-only tube was coated with a single layer of either CdS or PbS when the 2- and 3-layer structures were being coated as an independent check on the thickness for each layer.

### 3. Optical characterization of Ag/sulfide film HGWs

The spectral characteristics of the Ag/CdS and Ag/PbS HGWs were evaluated using a Perkin Elmer UV-VIS spectrometer and Nicolet Protégé FTIR. A typical spectral response shows interference peaks which depend on the thickness of the dielectric thin films. The thickness of a single layer dielectric,  $d$ , was calculated from the peak position of the longest-wavelength interference band,  $\lambda_p^{(m)}$ , using the relation [12],

$$d = \frac{m \cdot \lambda_p^{(m)}}{4 \cdot \sqrt{n_1^2 - 1}} \quad (1)$$

where  $m$  is the order of the interference maxima ( $m = 1$  for the longest-wavelength band);  $\lambda_p$  is the wavelength of the  $m^{\text{th}}$  absorption peak; and  $n_1$  is the refractive index of the dielectric film. From Eq. (1) we see that the peak position shifts to longer wavelengths as the thickness of the film increases. Spectral data has been used to determine the thickness of films prepared using different growth kinetics. The film thickness obtained from the optical measurements has then been correlated with direct thickness measurements using a field-emission scanning electron microscope (FESEM). In this way we obtain the growth kinetic curves for CdS and PbS deposited on Ag, shown in Fig. 1.

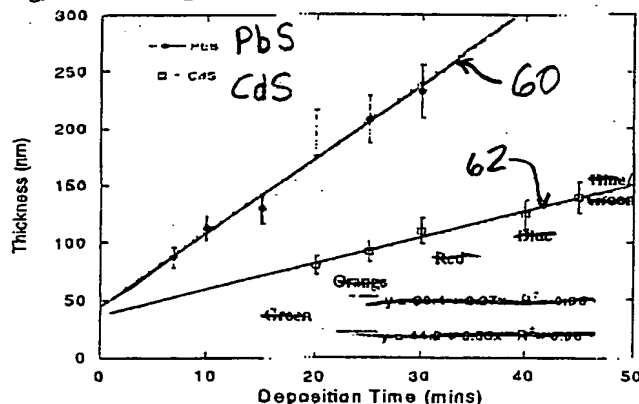


Fig. 1 The growth kinetic curves of the CdS and PbS thin films deposited in a Ag coated, 1,000  $\mu\text{m}$  bore HGWs. The color indicated is the color that one would see looking through the waveguides with an optical microscope.

FIG. 1

All films were prepared using 0.01 M solutions and a flow rate of 30 ml/min. The growth kinetics curves in Fig. 1 indicate that CdS (open symbols) has a slower growth rate on Ag compared to PbS (solid symbols) under similar conditions. The reason for the slower growth rate for CdS compared to PbS is that the CdS complexes with the ammonia used in the deposition and this decreases the rate of deposition. The data also show that the thickness of both dielectrics increases linearly with time, with growth rates of  $\sim 2.3$  and  $6.9$  nm/min for CdS and PbS, respectively. The mechanism for linear growth is based on the Stranski-Krastanov model of island-like growth [16]. This mechanism involves nucleation and growth and we are in the linear growth region. This information is important as we need to carefully control film thickness for single and multilayer structures. The UV-VIS spectra for the Ag/CdS is given in Fig. 2 and the FTIR spectra for the Ag/PbS in Fig. 3. The spectral data clearly show that the position of the interference peaks shifts to longer wavelengths as the thickness of the film increases as predicted by Eq. (1). We also note from the insert photos in Fig. 2 that the HGWs show a color variation. This is due to selective filtering of the input white light by the thin film coating (interference effect). This color variation is seen with the CdS coatings but not the PbS films as these films do not transmit well at visible wavelengths.

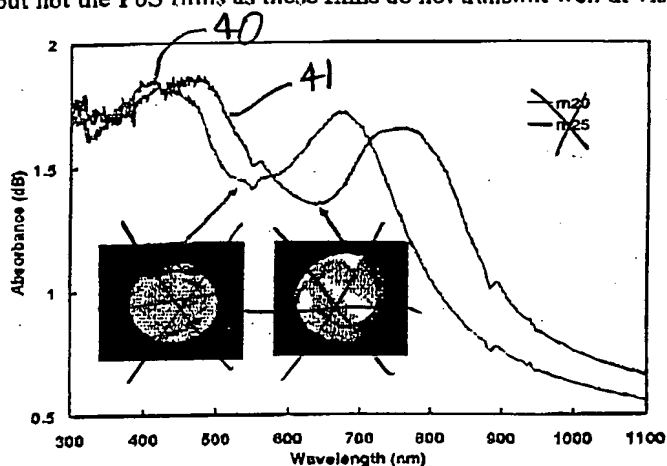


Fig. 2 UV-VIS spectra of 1,000- $\mu$ m bore Ag/CdS HGWs for different deposition times in minutes. The insert shows the color of the transmitted light as filtered by the coating.

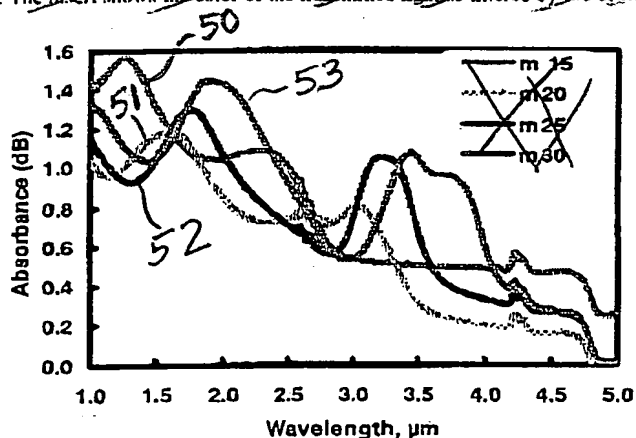


Fig. 3 FTIR spectra of 1,000- $\mu$ m bore Ag/PbS HGWs for different deposition times in minutes.

The thickness of the thin films was obtained by direct measurements using a FESEM. A photomicrograph taken with the FESEM for a typical cross-section of the thin film combination Ag/CdS/PbS is shown in Fig. 4. The CdS film appears darker than the PbS film because the in-lens detector produces a negative image of the secondary electron image. The thicknesses of the films shown in Fig. 4 are; Ag 154 nm, CdS  $169 \pm 16$  nm, PbS  $82 \pm 6$  nm. We do not see any degradation of the underlying film when the new film is deposited over it. That is, CdS and PbS do not react with each other during the deposition of successive layers. The film thickness measured from the FESEM micrographs of both single and multilayer dielectric film are summarized in Table 1. These results agree very well with the optical thickness measurement.

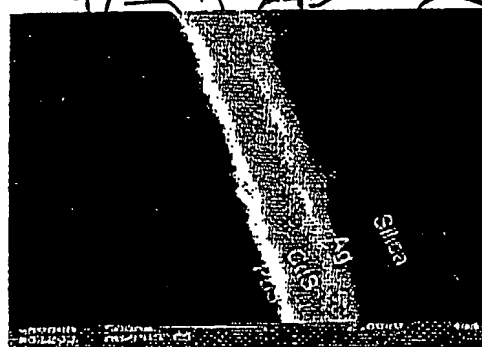


Fig. 4 Cross-sectional FESEM image of a 1,000- $\mu$ m bore Ag/CdS/PbS HGW. The CdS and PbS thin films are deposited sequentially inside the Ag coated HGW.

Table 1 Thickness values for CdS and PbS thin films on Ag determined from FESEM images

HGWs	Thickness of Ag nm	Thickness of CdS nm	Thickness of PbS nm
Ag/CdS	$156 \pm 16$	$172 \pm 16$	—
Ag/PbS	$158 \pm 20$	—	$96 \pm 16$
Ag/CdS/PbS	154	169	$82 \pm 6$

A series of 1,000- $\mu$ m bore HGWs with 1, 2, and 3 dielectric layers deposited over Ag were fabricated using wet chemistry methods [8, 11]. The spectral losses for these straight waveguides are shown in Fig. 5. From Fig. 5, it may be seen that the addition of each dielectric layer shifts the interference peaks to longer wavelengths. This is a result of the increase in thickness with each additional layer.

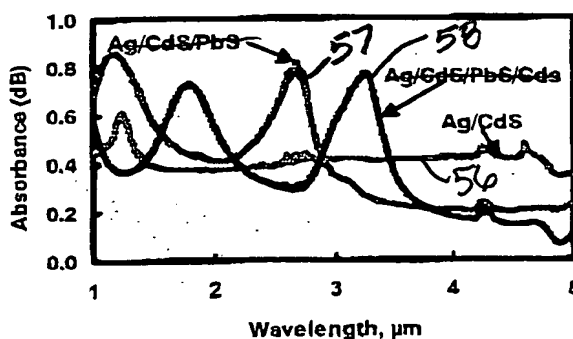
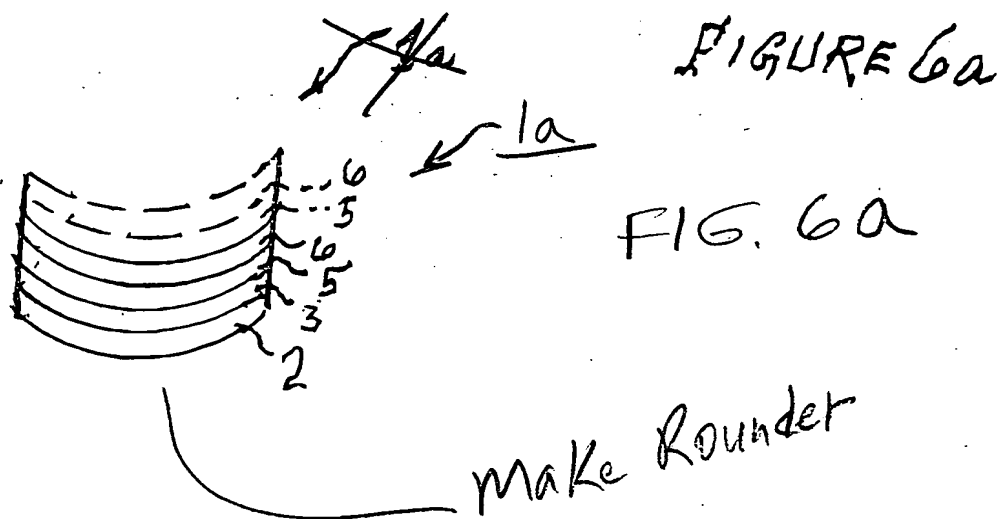
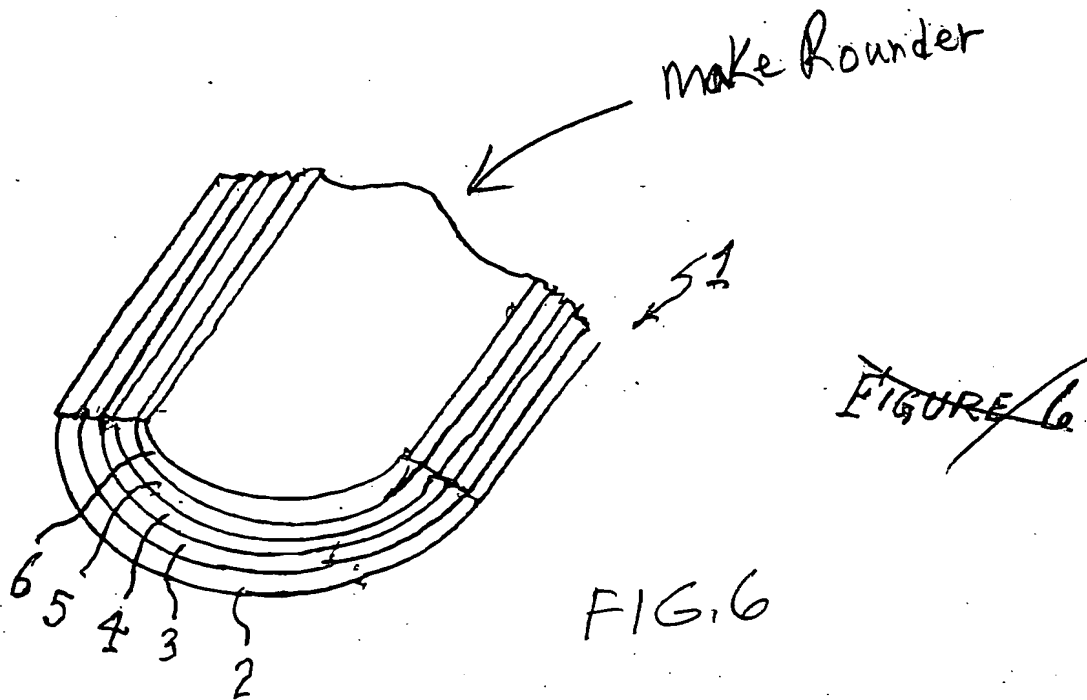


Fig. 5 FTIR Spectra of a 1,000- $\mu$ m bore of 1, 2, and 3-layer dielectric coatings on Ag coated HGWs. The spectra beyond 4 to 12  $\mu$ m region are essentially flat and featureless.





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